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Electronic Supporting Information (ESI)

for

Two microporous Fe-based MOFs with multiple active sites for selective gas adsorption

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S1. Experimental Section

Materials and methods.

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 II analyzer (Perkin-Elmer, USA). The X-ray powder diffraction (XRPD) was obtained on a D/MAX-rA (Rigaku) diffractometer with Cu K_α radiation ($\lambda = 1.542$ Å) with a scan rate of $4^\circ\ \mathrm{min}^{-1}$. The tube voltage and current are 36 kV and 20 mA, respectively. FT-IR spectra were recorded on a FT6700 spectrometer (USA) using KBr disc method in the range of 400–4000 cm^{-1}. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org.

Syntheses of LCU-101 and LCU-102:

$[Fe_2(BPDC)(DMAC)_3]_n$ (LCU-101): A mixture of $FeCl_3$ (65 mg, 0.4 mmol), H_4BPDC (66 mg, 0.2 mmol), and 2,6-dimethylpyridine (0.20 mL) in 10 mL DMAC (10 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 160 °C for 4 days and then cooled to room temperature at a rate of 10 $°C·h^{-1}$. Block-like yellow crystals of **LCU-101** were collected. Yield: 22% for **LCU-101** based on Fe, respectively. Elemental analysis (%) for activated sample **LCU-101a**, $C_{16}H_6O_8Fe_2$ (M = 437.90): *Calcd.*: C, 43.88; H, 1.38; *Found*: C, 43.15; H, 1.22. IR (KBr disk, cm^{-1}) see Fig. S6 in ESI.

$\{[H_2N(CH_3)_2][Fe_2Na_3(BPDC)_2(DMAC)_2(H_2O)]·DMAC\}_n$ (LCU-102): A mixture of $FeCl_3·6H_2O$ (65 mg, 0.24 mmol), H_4BPDC (66 mg, 0.2 mmol), NaOH (40 mg, 1 mmol) and 2,6-dimethylpyridine (0.20 mL) in 10 mL DMAC (10 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 160 °C for 4 days and then cooled to room temperature at a rate of 10 $°C·h^{-1}$. Block-like yellow crystals of **LCU-102** were collected. Yield: 20% for **LCU-102** based on Fe, respectively. Elemental analysis (%) for **LCU-102**, $C_{46}H_{49}O_{20}N_4Na_3Fe_2$ (M = 1158.56): *Calcd.*: C, 47.69; H, 4.26; N, 4.84; *Found*: C, 47.21; H, 3.85; N, 4.32. IR (KBr disk, cm^{-1}) see Fig. S7 in ESI.

X-ray Crystallography.

The crystallographic data of **LCU-101** and **LCU-102** were collected on a Rigaku SCX-mini diffractometer and Bruker SMART at 298(2) K with Mo-Kα radiation (λ = 0.71073 Å), respectively. The crystal data were solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[S1] Fe and Na atoms in **LCU-101** and **LCU-102** were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms of organic ligands were added theoretically, riding on the concerned atoms and refined with fixed thermal factors.

During the refinement of the two compounds, the command "omit -3 50" was used to omit some disagreeable reflections. The command "dfix" was used to fix some bonds. For **LCU-101**, the command "delu" was used to solve the alert of "Large Hirshfeld Difference...". The atoms C40, C50, C51, C52, C54, C64 and C65 were restrained using thermal restraints (isor) to sovle ADP or NDP alerts and make the displacement parameters more reasonable. It should be noted that some guest molecules (DMAC) in the channels of **LCU-101** are highly disordered and could not be modeled properly, so the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON[S2] and the results were appended to the bottom of the CIF file. For **LCU-102**, the command "simu" was used to solve the alert of "Large Hirshfeld Difference...". The atoms N3, O19, C37, C44, C45, C46, C47, C51, C39 and C49 were restrained using thermal restraints (isor and simu) to sovle ADP or NDP alerts and make the displacement parameters more reasonable. The H atoms of the coordinated water molecules in **LCU-102** cannot be added in the calculated positions, and they were directly included in the final molecular formula. Due to the limited crystal quality, the more solvents, and the relatively high "restraints" in the **LCU-102**, which all result the higher *R* value. Further details of crystal data and structure refinement for **LCU-101** and **LCU-102** were summarized as follows in Table S1. Selected bond lengths of **1** and **2** were given in Table S2 and Table S3. Full crystallographic data for **LCU-101** and **LCU-102** have been deposited with the CCDC (1486513 for **LCU-101**, and 1486514 for **LCU-102**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.[S3]

References

S1. (a) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

S2. A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Untrecht University, 2003.

S3. The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.

Crystal data for LCU-101 and LCU-102

Table S1. Crystal Data and Structure Refinement Parameters for Compounds LCU-101 and LCU-102.

Compounds	**LCU-101**	**LCU-102**
Formula	$C_{28}H_{33}O_{11}N_3Fe_2$	$C_{46}H_{49}O_{20}N_4Na_3Fe_2$
F_w	699.27	1158.56
λ/Å	0.71073	0.71073
T/K	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P21/c$	$P21/c$
a [Å]	18.698(7)	13.5430(12)
b [Å]	19.292(7)	19.3401(17)
c [Å]	19.383(7)	23.223(2)
α[°]	90	90
β [°]	91.045(4)	123.452(3)
γ[°]	90	90
V (Å^3)	6991(4)	5075.0(8)
Z	4	4
D_c/Mg·m^{-3}	1.329	1.514
F(000)	2895	2384
Reflections collected/unique	52502/12280	24197/8926
R_{int}	0.1799	0.1569
Data/Restraints/Parameters	12280/53/811	8926/190/716
R_1/wR_2 [I>2σ(I)] ^{a}	0.1307/0.3411	0.0891/0.2247
R_1/wR_2 [(all data)] ^{a}	0.1715/0.3758	0.2013/0.2693
GOF on F^2	1.097	0.917

^{a} $R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$ $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

Sorption measurements.

Gas adsorption/desorption measurements were carried out using a Micrometrics ASAP 2020M volumetric gas adsorption instrument. UHP-grade gases were used in measurements. Before the measurement, the samples of **LCU-101** and **LCU-102** were soaked in anhydrous methanol (CH_3OH) for 3 days to remove DMAC solvent molecules in the channels, and then filtrated, and activation of the methanol-exchanged **LCU-101** and **LCU-102** at 120 °C under high vacuum (less than 10^{-5} Torr) overnight led to the formation of activated sample **LCU-101a** and **LCU-102a**. About 180 mg (for **LCU-101**) and 190 mg (for **LCU-102**) of the desolvated samples were used for the entire adsorption/desorption measurements. The Ar adsorption/desorption isotherm measurements were proceeded at 77 K in a liquid nitrogen bath. The H_2 adsorption/desorption isotherms were collected at 77 K in a liquid nitrogen bath and 87 K in a liquid argon bath. The CO_2, CH_4 and N_2 adsorption/desorption isotherm measurements were carried out at 273 K in an ice-water bath, respectively.

S2. Figures in Supporting Information

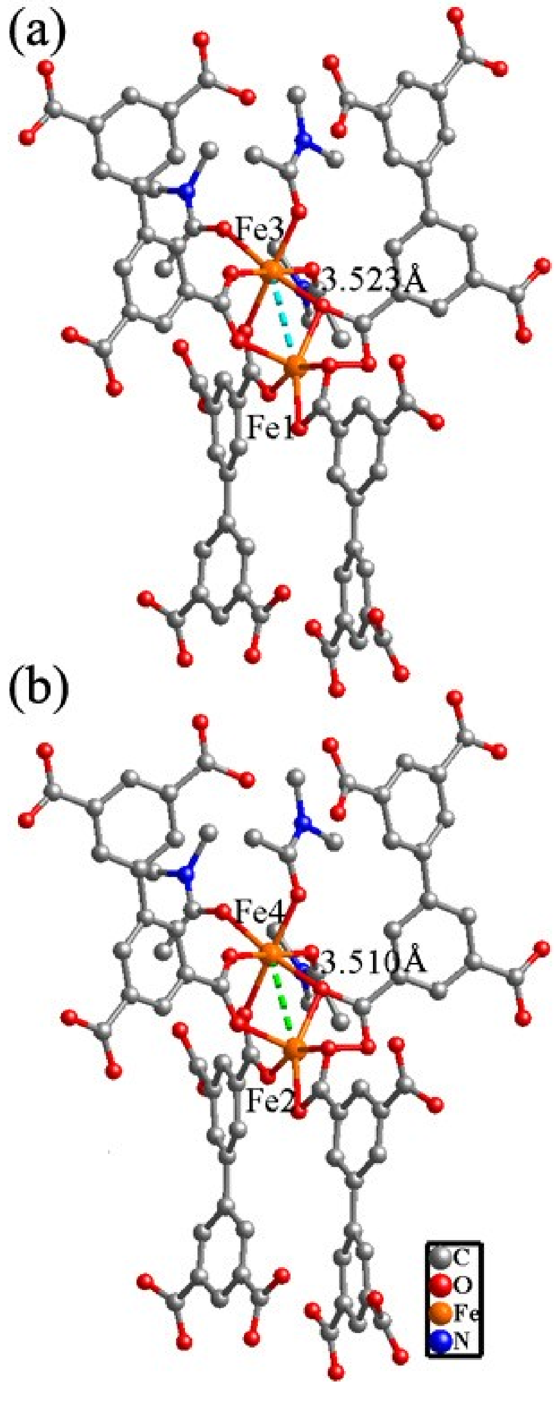

Fig. S1 The different Fe···Fe distances of the two adjacent dimeric Fe-clusters for **LCU-101**.

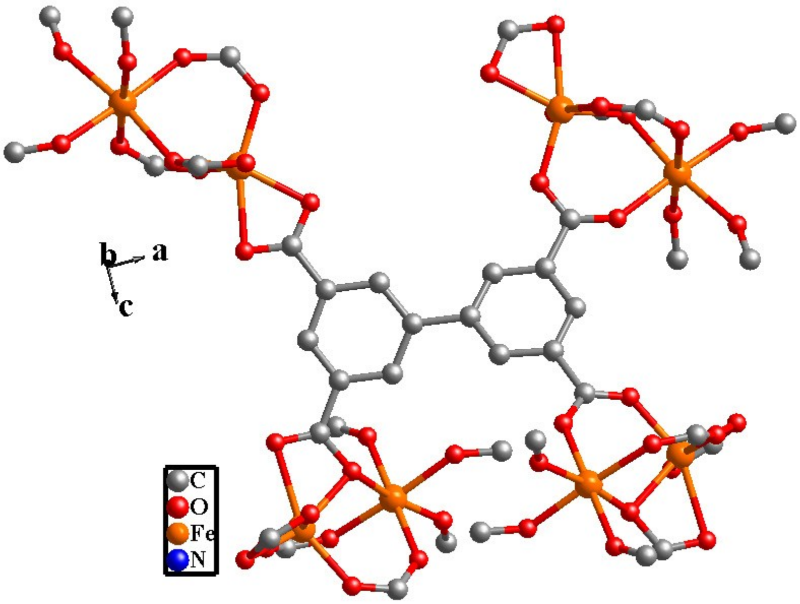

Fig. S2 The coordination mode of the ligand for **LCU-101**.

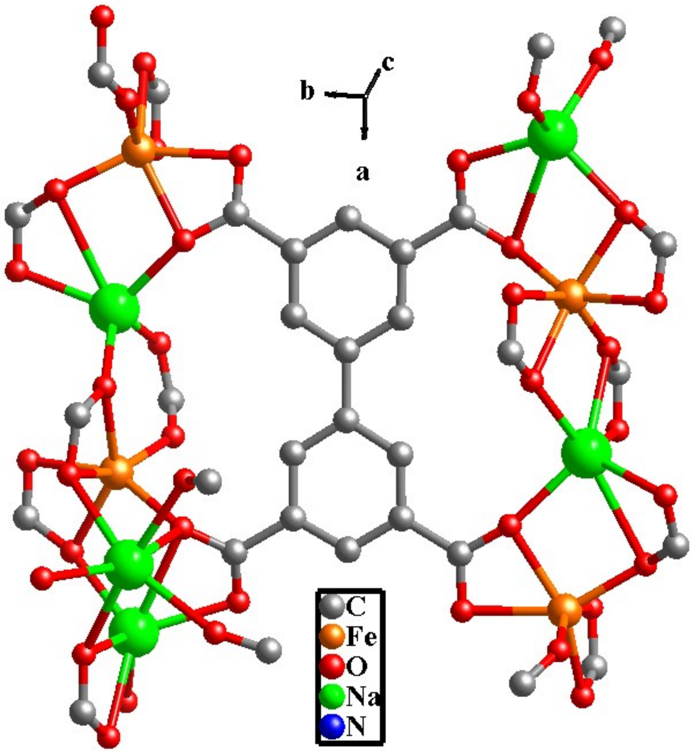

Fig. S3 The coordination mode of the ligand for **LCU-102**.

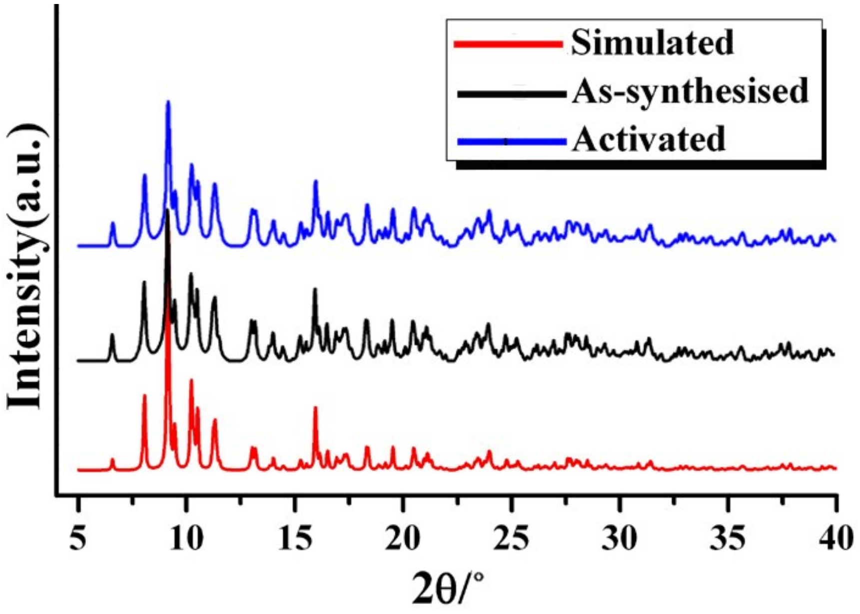

Fig. S4 XRPD patterns for **LCU-101** and **LCU-101a**.

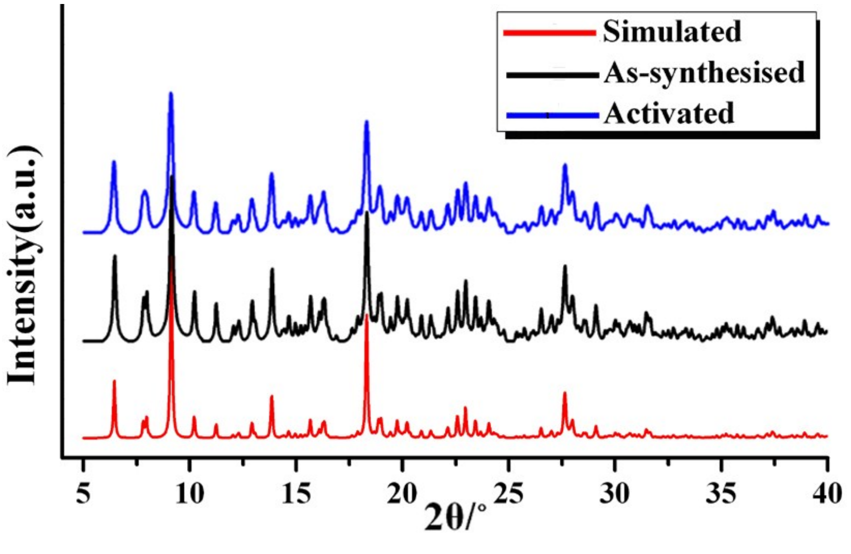

Fig. S5 XRPD patterns for **LCU-102** and **LCU-102a**.

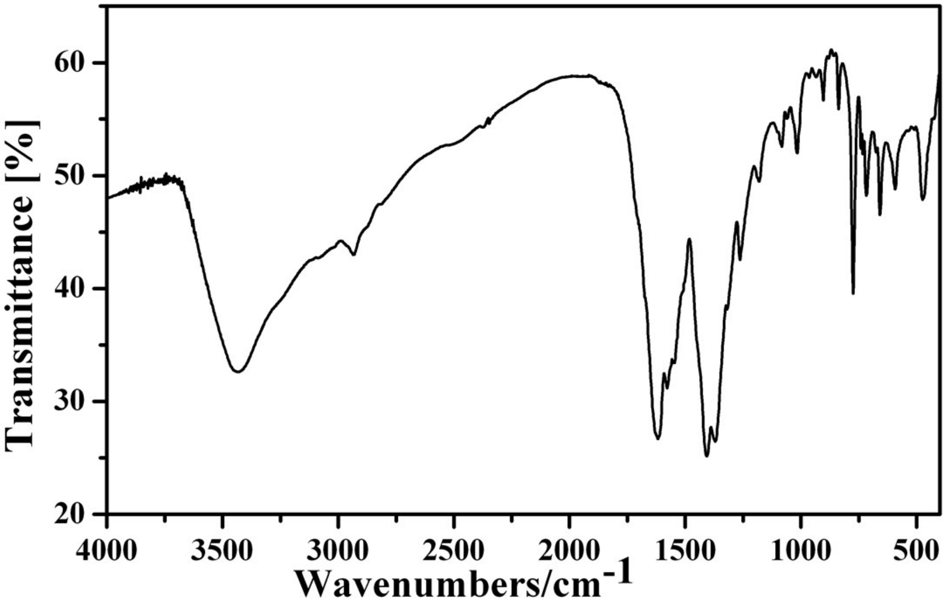

Fig. S6 IR spectra of compound **LCU-101**.

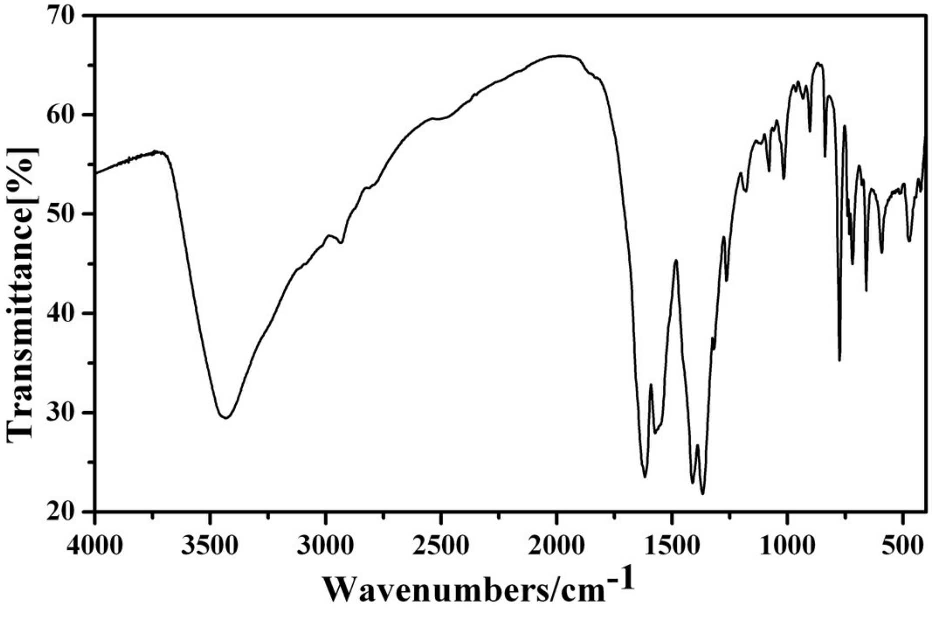

Fig. S7 IR spectra of compound **LCU-102**.

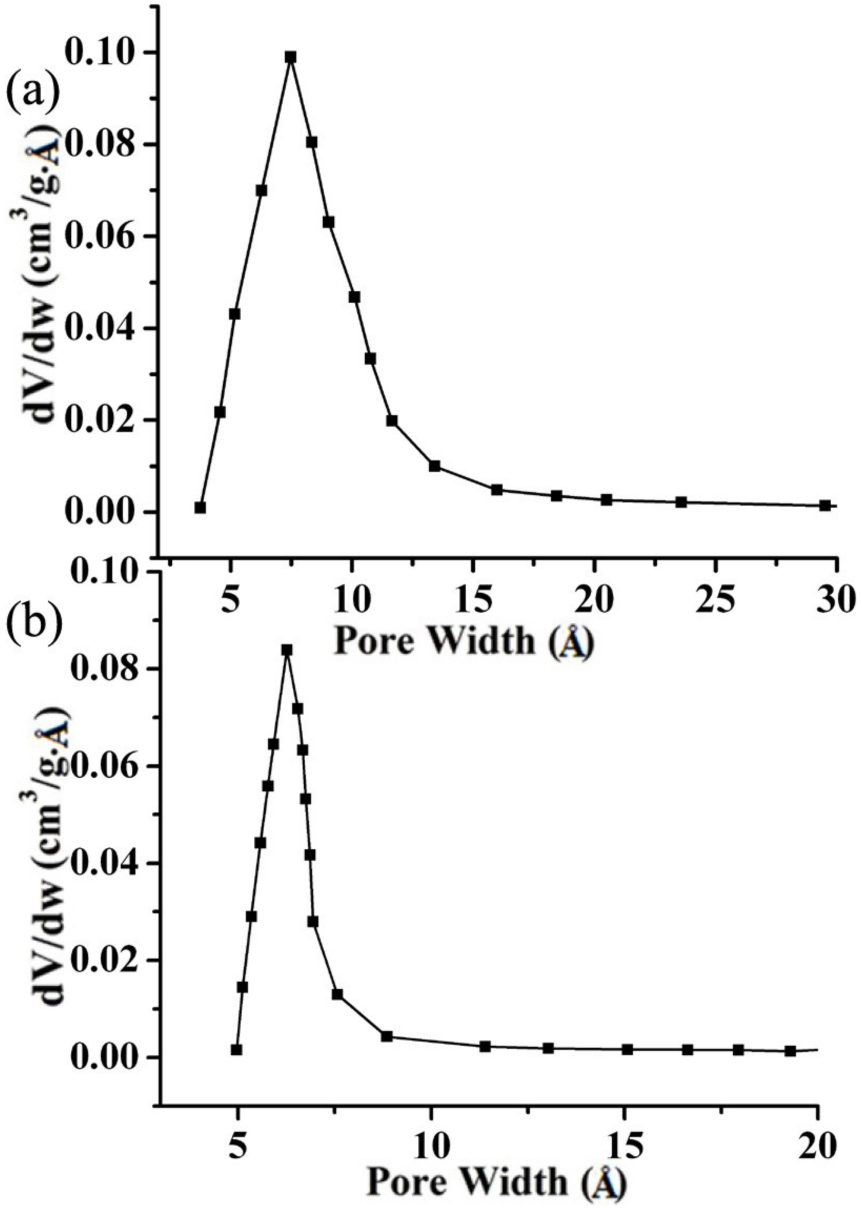

Fig. S8 Pore size distribution of **LCU-101a** and **LCU-102a**.

The study of hydrogen storage.

As one of energy carrier gas of interest, the H_2 adsorption of **LCU-101a** and **LCU-102a** should also be examined. The results show that the H_2 uptake of **LCU-101a** and **LCU-102a** at 77 K reaches *ca.* 88.8 cm^3/g (STP) and 80.5 cm^3/g (STP), respectively, see Fig. 3a and 3b. This storage capacity can be comparable to that of many previously reported MOFs under similar conditions.[S4-S5] In addition, the H_2 adsorption enthalpies were also estimated using the H_2 isotherms at 77 and 87 K by virial equation.[S4-S5] The calculated Q_{st} values are 9.2~10.6 kJ/mol for **LCU-101a** (Fig. S9a) and 8.5~6.9 kJ/mol for **LCU-102a** (Fig. S9b), which are also comparable to many reported MOFs.[S4-S5]

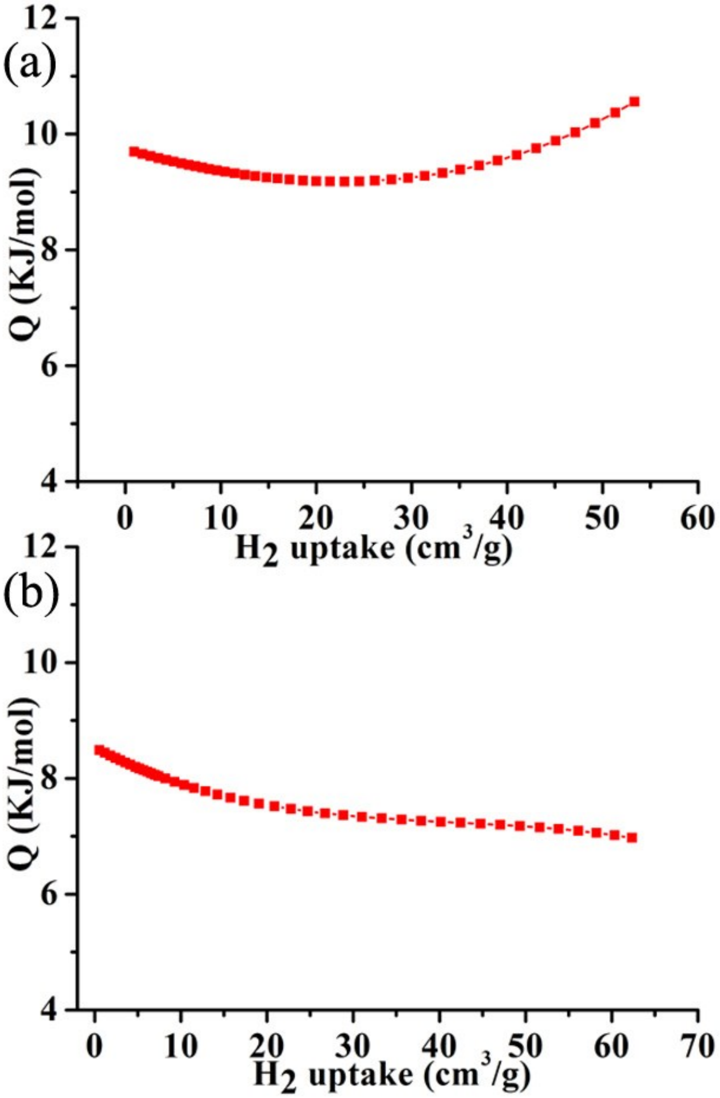

Fig. S9 H_2 adsorption enthalpy for **LCU-101a** and **LCU-102a** calculated from the H_2 adsorption isotherms at 77 K and 87 K.

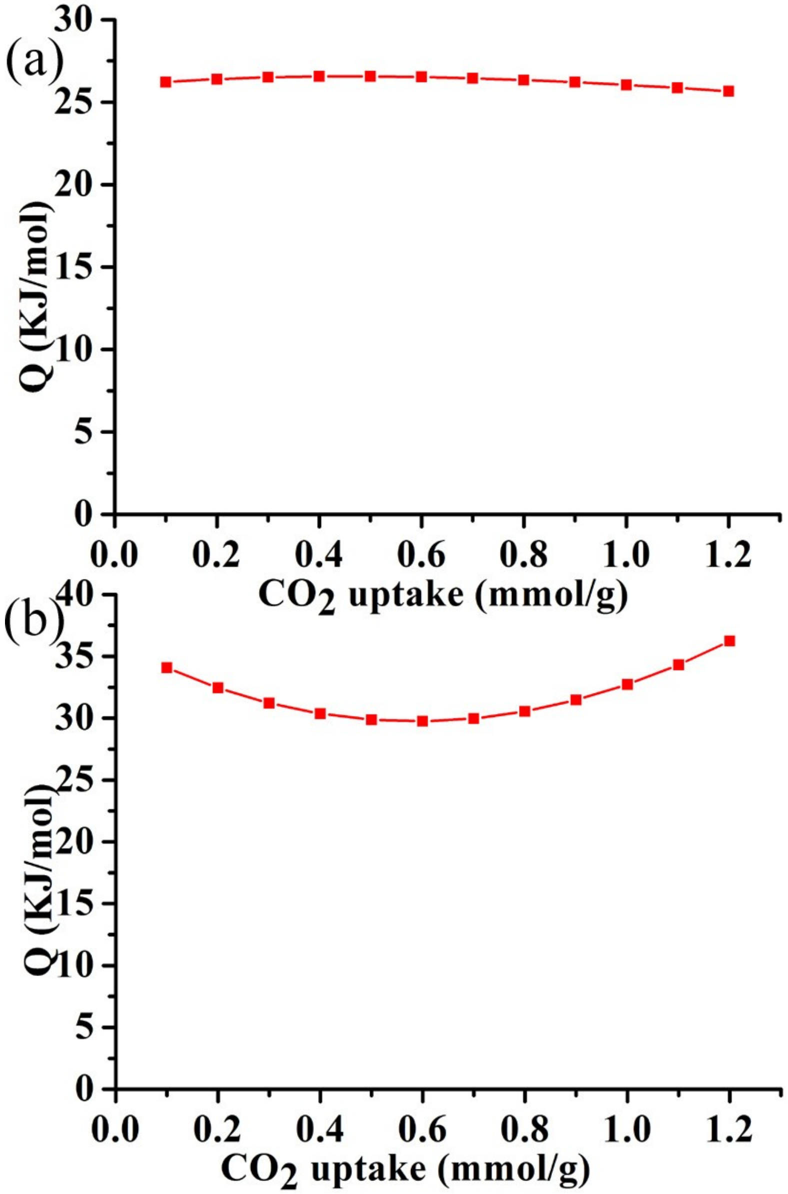

Fig. S10 CO_2 adsorption enthalpy for **LCU-101a** and **LCU-102a** calculated from the CO_2 adsorption isotherms at 273 K, 283 K and 298 K.

S4 X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2009, **131**, 2159−2171.

S5 (a) A. J. Lan, K. H. Li, H. H. Wu, L. Z. Kong, N. Nijem, D. H. Olson, T. J. Emge, Y. J. Chabal, D. C. Langreth, M. C. Hong and J. Li, *Inorg. Chem.*, 2009, **48**, 7165−7173; (b) D. C. Zhong, J. B. Lin, W. G. Lu, L. Jiang and T. B. Lu, *Inorg. Chem.*, 2009, **48**, 8656−8658.

S3. IAST adsorption selectivity calculation:[S5-S7]

The experimental isotherm data for pure CO_2, CH_4 and N_2 (measured at 273 K) were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * p^{c}}{1 + b * P^{c}}$$

Where q and p are adsorbed amounts and pressures of component i, respectively.
Using the pure component isotherm fits, the adsorption selectivity is defined by

$$S_{ads} = \frac{q_1 / q_2}{p_1 / p_2}$$

Where q_i is the amount of i adsorbed and p_i is the partial pressure of i in the mixture.
We used the following written codes to simulate the adsorption selectivity of CO_2 over CH_4 or N_2 in Fig. 4 and S11, S12:

28 # No. of Pressure Point

y1, y2 # Molar fraction of binary mixture (y1 and y2, y1 + y2 = 1)

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109 #The unit is same parameter b, kPa

a1, a2 # fitting parameter Nsat (A1) for both component (Unit: mmol/g)

b1, b2 # fitting parameter b1 for both components (Unit: kPa^{-1})

c1, c2 # fitting parameter c1 for both components

0, 0 # fitting parameter Nsat2(A2) for both component(Unit: mmol/g)

0, 0 # fitting parameter b2 for both components (Unit: kPa^{-1})

1, 1 # fitting parameter c2 for both components

S6 F. Daniels, R. A. Alberty, J. W. Williams, C. D. Cornwell, P. Bender and J. E. Harriman, *Experimental Physical Chemistry, 6th Ed, McGraw-Hill Book Co. Inc.*, New York, **1962**.

S7 M. Dincă and J. R. Long, *J. Am. Chem. Soc.,* 2005, **127**, 9376−9377.

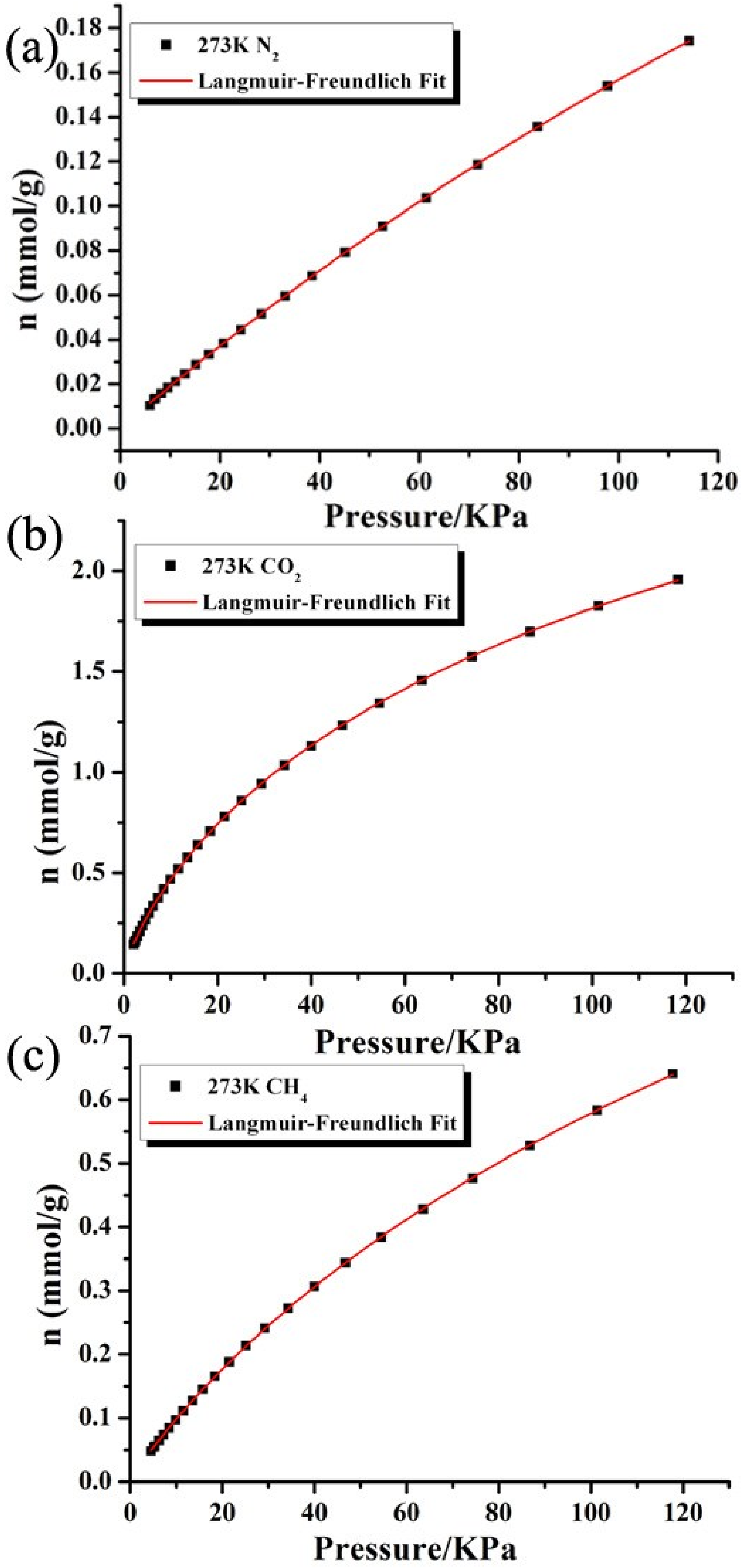

Fig. S11 N_2, CO_2 and CH_4 adsorption isotherms of **LCU-101a** with fitting by L-F model.

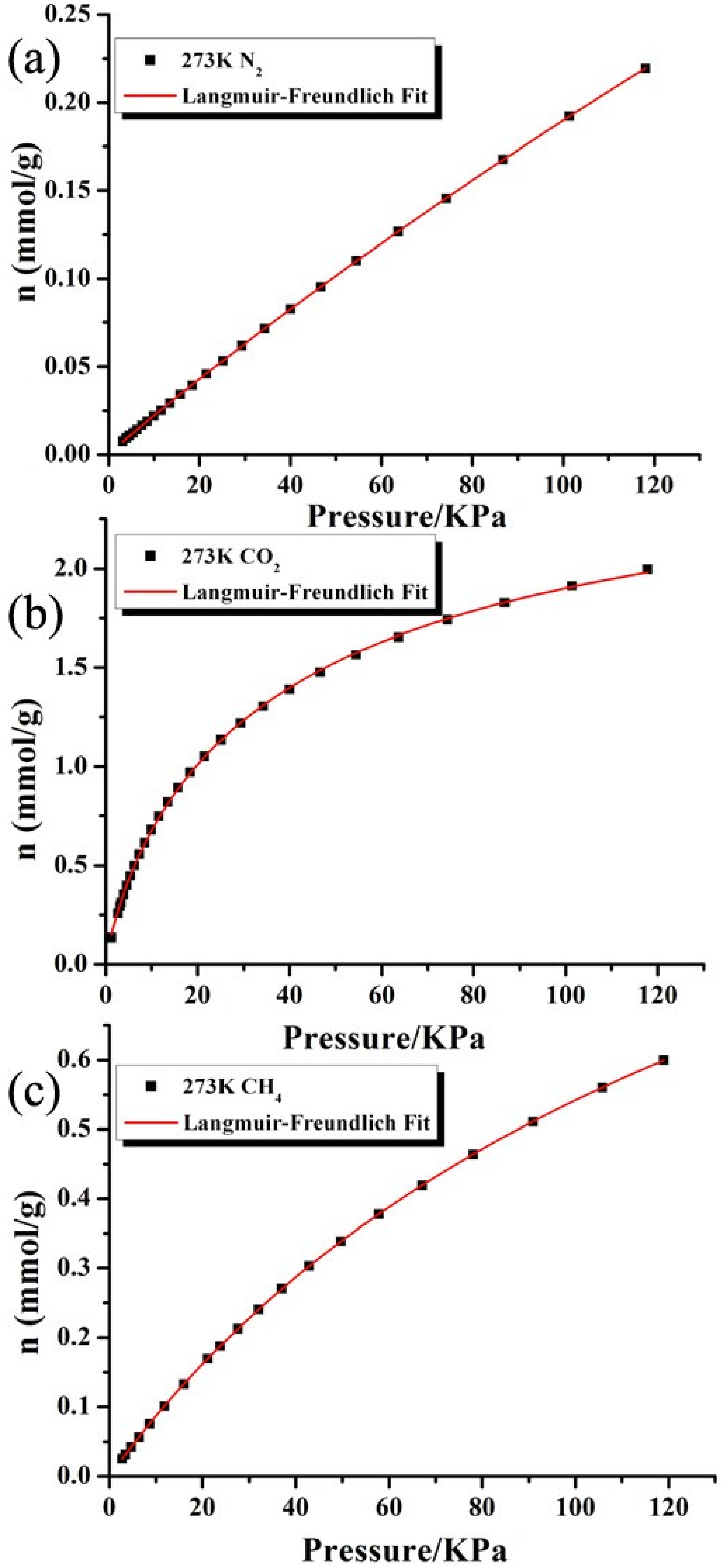

Fig. S12 N_2, CO_2 and CH_4 adsorption isotherms of **LCU-102a** with fitting by L-F model.

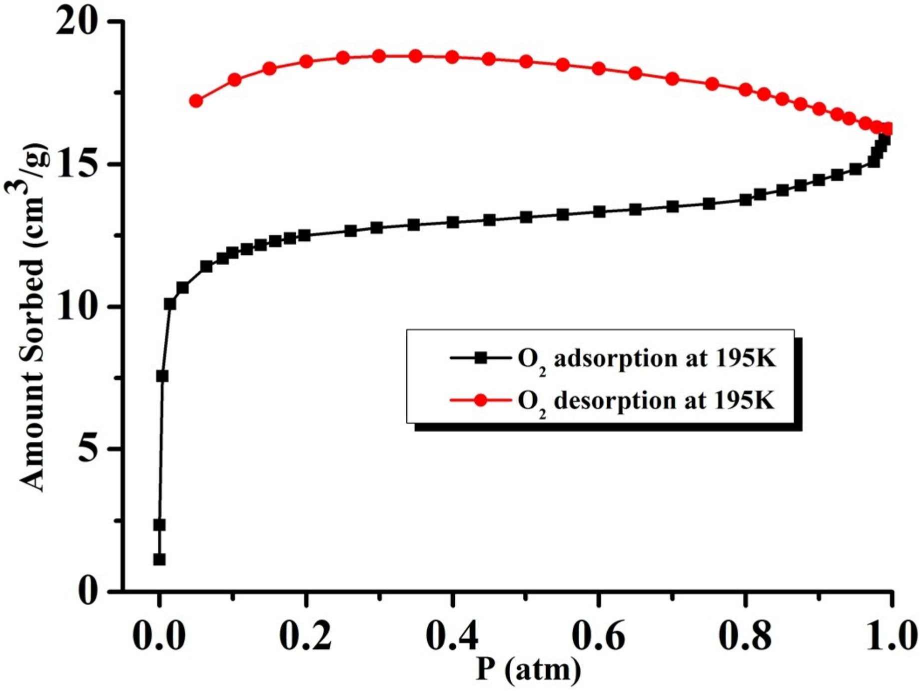

Fig. S13 O_2 sorption isotherms for **LCU-101a**.

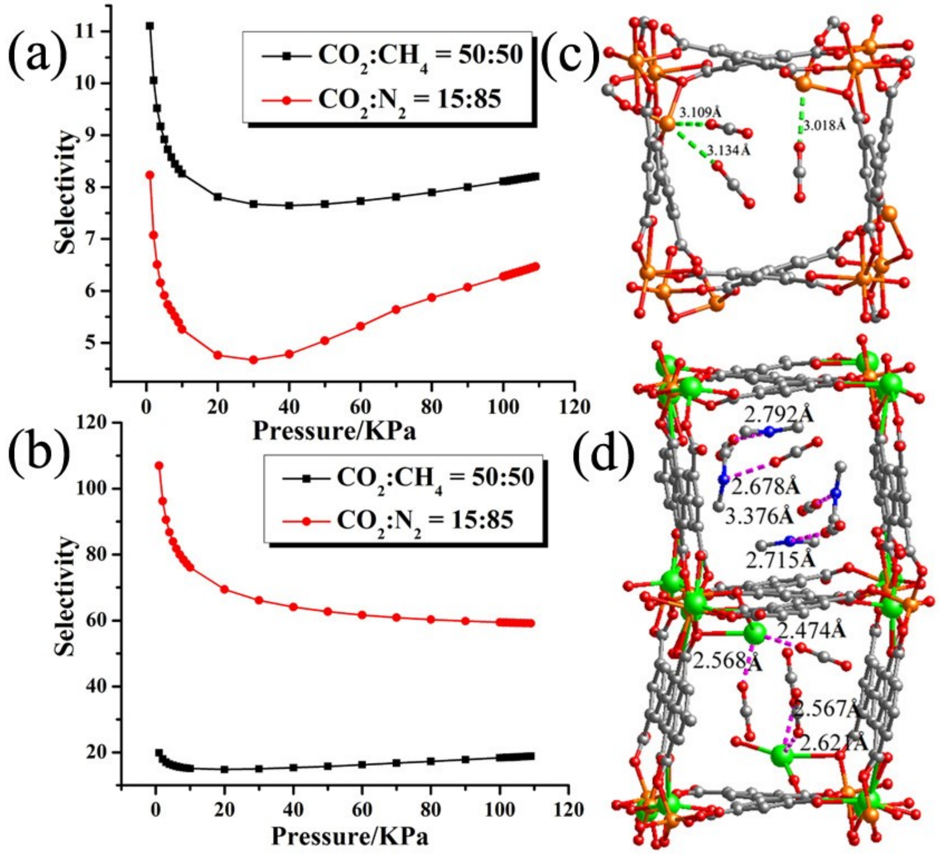

Fig. S14 IAST adsorption selectivities of (a) **LCU-101a** and (b) **LCU-102a**; (c) (d) preferential CO_2 binding sites simulated with GCMC.

S4 The computational simulation studies of gases adsorption

To further investigate interactions between CO_2 molecules and the **LCU- 101** and **LCU-10**2, grand canonical Monte Carlo (GCMC) simulations were carried out using the Sorption module of Materials Studio 5.0 package.[S7] The Locate and Metropolis methods[S8] were used to predict the possible binding sites of CO_2 molecules onto the frameworks. The unit cell frameworks of **LCU-101** and **LCU-102** were constructed from experimental crystal X-ray diffraction data. The loading number of CO_2 adsorbed onto each unit cell of the two kinds of frameworks was choose as 20 based on our experimental data. During the simulation, the CO_2 and dimethylamine molecules including the frameworks were considered as rigid, and periodic boundary conditions were applied in all three directions. The interaction energy between CO_2 and frameworks were calculated by the Coulomb and Lennard-Jones 6-12 (LJ) potentials. A cutoff radius of 12.5 Å for the LJ potentials was used throughout the simulation. All parameters including the partial charges were assigned by the COMPASS force field[S9] embedded in the Sorption module.

S8 *Accelrys*, *Materials Studio Getting Started, release 5.0; Accelrys Software*, Inc.: San Diego, CA, 2009.

S9 N. Metropolis and S. Ulam, *J. Am. Stat.l Assoc.*, 1949, **60**, 115−129.

S10 H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338−7364.

S5. The selected bond lengths [Å] and angles [º] of compounds LCU-101 and LCU-102.

Table S2 The selected bond lengths [Å] and angles [º] of compound **LCU-101**.

O(8)-Fe(1)#1	2.124(6)	Fe(3)-O(9)	2.113(6)
O(8)-Fe(3)#1	2.184(6)	Fe(3)-O(8)#1	2.184(6)
O(22)-Fe(3)	2.169(9)	Fe(3)-O(18)	2.204(8)
O(7)-Fe(1)#1	2.360(8)	Fe(4)-O(21)	2.093(7)
Fe(1)-O(10)	1.998(6)	Fe(4)-O(12)#4	2.096(7)
Fe(1)-O(2)	2.014(7)	Fe(4)-O(3)#3	2.107(6)
Fe(1)-O(8)#1	2.124(6)	Fe(4)-O(26)	2.139(8)
Fe(1)-O(15)#2	2.156(6)	Fe(4)-O(20)	2.179(8)
Fe(1)-O(16)#2	2.200(7)	Fe(4)-O(13)	2.187(7)
Fe(2)-O(4)#3	2.017(6)	O(3)-Fe(4)#6	2.107(6)
Fe(2)-O(11)#4	2.075(6)	O(4)-Fe(2)#6	2.017(6)
Fe(2)-O(13)	2.102(6)	O(5)-Fe(2)#7	2.102(6)
Fe(2)-O(5)#5	2.102(6)	O(11)-Fe(2)#4	2.075(6)
Fe(2)-O(6)#5	2.259(8)	O(15)-Fe(1)#2	2.156(6)
Fe(2)-O(14)	2.326(7)	O(6)-Fe(2)#7	2.259(8)
Fe(3)-O(17)	2.059(6)	O(12)-Fe(4)#4	2.096(7)
Fe(3)-O(1)	2.082(7)	O(16)-Fe(1)#2	2.200(7)
O(10)-Fe(1)-O(2)	95.6(3)	O(4)#3-Fe(2)-O(14)	94.7(3)
O(10)-Fe(1)-O(8)#1	101.6(3)	O(11)#4-Fe(2)-O(14)	154.1(2)
O(2)-Fe(1)-O(8)#1	96.6(2)	O(13)-Fe(2)-O(14)	59.6(2)
O(10)-Fe(1)-O(15)#2	157.3(3)	O(5)#5-Fe(2)-O(14)	90.7(3)
O(2)-Fe(1)-O(15)#2	94.7(3)	O(6)#5-Fe(2)-O(14)	83.6(3)
O(8)#1-Fe(1)-O(15)#2	97.3(2)	O(17)-Fe(3)-O(1)	92.1(3)
O(10)-Fe(1)-O(16)#2	97.3(3)	O(17)-Fe(3)-O(9)	174.0(3)
O(2)-Fe(1)-O(16)#2	100.0(3)	O(1)-Fe(3)-O(9)	93.5(3)
O(8)#1-Fe(1)-O(16)#2	153.4(3)	O(17)-Fe(3)-O(22)	88.6(3)
O(15)#2-Fe(1)-O(16)#2	60.9(2)	O(1)-Fe(3)-O(22)	178.6(3)
O(10)-Fe(1)-O(7)#1	94.5(3)	O(9)-Fe(3)-O(22)	85.7(3)
O(2)-Fe(1)-O(7)#1	155.4(2)	O(17)-Fe(3)-O(8)#1	89.5(2)
O(8)#1-Fe(1)-O(7)#1	59.3(2)	O(1)-Fe(3)-O(8)#1	88.0(2)
O(15)#2-Fe(1)-O(7)#1	84.3(3)	O(9)-Fe(3)-O(8)#1	92.8(2)
O(16)#2-Fe(1)-O(7)#1	100.9(3)	O(22)-Fe(3)-O(8)#1	93.2(3)
O(4)#3-Fe(2)-O(11)#4	93.4(3)	O(17)-Fe(3)-O(18)	83.4(3)
O(4)#3-Fe(2)-O(13)	104.3(3)	O(1)-Fe(3)-O(18)	92.2(3)
O(11)#4-Fe(2)-O(13)	94.5(2)	O(9)-Fe(3)-O(18)	94.2(3)
O(4)#3-Fe(2)-O(5)#5	100.4(3)	O(22)-Fe(3)-O(18)	86.7(4)
O(11)#4-Fe(2)-O(5)#5	111.9(3)	O(8)#1-Fe(3)-O(18)	172.9(2)
O(13)-Fe(2)-O(5)#5	142.4(3)	O(21)-Fe(4)-O(12)#4	89.8(3)
O(4)#3-Fe(2)-O(6)#5	160.5(3)	O(21)-Fe(4)-O(3)#3	177.0(3)
O(11)#4-Fe(2)-O(6)#5	96.5(3)	O(12)#4-Fe(4)-O(3)#3	92.0(3)
O(13)-Fe(2)-O(6)#5	91.7(3)	O(21)-Fe(4)-O(26)	89.5(3)
O(5)#5-Fe(2)-O(6)#5	60.3(3)	O(12)#4-Fe(4)-O(26)	177.3(3)

O(21)-Fe(4)-O(20)	82.7(3)	O(3)#3-Fe(4)-O(26)	88.7(3)
O(12)#4-Fe(4)-O(20)	93.1(4)	O(12)#4-Fe(4)-O(13)	86.9(3)
O(3)#3-Fe(4)-O(20)	94.9(3)	O(3)#3-Fe(4)-O(13)	93.9(3)
O(26)-Fe(4)-O(20)	89.5(4)	O(26)-Fe(4)-O(13)	90.4(3)
O(21)-Fe(4)-O(13)	88.5(3)	O(20)-Fe(4)-O(13)	171.2(3)

Symmetry transformations used to generate equivalent atoms: #1: -x+2, -y+2, -z+1; #2: -x+1, -y+2, -z+1; #3: -x+1, y-1/2, -z+3/2; #4 -x+1, -y+1, -z+1; #5: x-1, -y+3/2, z-1/2; #6: -x+1, y+1/2, -z+3/2; #7: x+1, -y+3/2, z+1/2.

Table S3 The selected bond lengths [Å] and angles [º] of compound **LCU-102**.

Fe(2)-O(3)	1.949(6)	Fe(1)-O(14)#6	2.144(6)
Fe(2)-O(15)#1	1.975(7)	Fe(1)-O(2)	2.150(6)
Fe(2)-O(11)	2.119(6)	Fe(1)-O(13)#6	2.186(6)
Fe(2)-O(5)#2	2.165(6)	Fe(1)-O(1)	2.196(6)
Fe(2)-O(6)#2	2.170(6)	O(13)-Fe(1)#7	2.186(6)
Fe(2)-O(12)	2.228(6)	O(14)-Fe(1)#7	2.144(6)
O(7)-Fe(1)#4	2.006(6)	O(6)-Fe(2)#8	2.170(6)
Fe(1)-O(10)	1.980(7)	O(5)-Fe(2)#8	2.165(6)
Fe(1)-O(7)#5	2.006(6)	O(15)-Fe(2)#9	1.975(7)
O(3)-Fe(2)-O(15)#1	98.7(3)	O(10)-Fe(1)-O(7)#5	95.3(3)
O(3)-Fe(2)-O(11)	114.1(3)	O(10)-Fe(1)-O(14)#6	96.4(3)
O(15)#1-Fe(2)-O(11)	87.8(3)	O(7)#5-Fe(1)-O(14)#6	110.7(3)
O(3)-Fe(2)-O(5)#2	150.3(3)	O(10)-Fe(1)-O(2)	104.4(3)
O(15)#1-Fe(2)-O(5)#2	92.5(3)	O(7)#5-Fe(1)-O(2)	92.0(2)
O(11)-Fe(2)-O(5)#2	93.6(2)	O(14)#6-Fe(1)-O(2)	147.6(2)
O(3)-Fe(2)-O(6)#2	90.9(3)	O(10)-Fe(1)-O(13)#6	154.3(3)
O(15)#1-Fe(2)-O(6)#2	112.7(3)	O(7)#5-Fe(1)-O(13)#6	86.4(2)
O(11)-Fe(2)-O(6)#2	145.4(2)	O(14)#6-Fe(1)-O(13)#6	59.5(2)
O(5)#2-Fe(2)-O(6)#2	59.4(2)	O(2)-Fe(1)-O(13)#6	101.1(2)
O(3)-Fe(2)-O(12)	96.2(3)	O(10)-Fe(1)-O(1)	95.9(3)
O(15)#1-Fe(2)-O(12)	146.9(3)	O(7)#5-Fe(1)-O(1)	150.5(3)
O(11)-Fe(2)-O(12)	59.1(2)	O(14)#6-Fe(1)-O(1)	95.0(3)
O(5)#2-Fe(2)-O(12)	88.9(3)	O(2)-Fe(1)-O(1)	58.8(2)
O(6)#2-Fe(2)-O(12)	96.4(2)	O(13)#6-Fe(1)-O(1)	94.9(3)

Symmetry transformations used to generate equivalent atoms: #1: x, -y+1/2, z+1/2; #2: -x+1, y-1/2, -z+1/2; #3: x-1, y, z; #4: -x+2, y+1/2, -z+1/2; #5: -x+2, y-1/2, -z+1/2; #6: x+1, -y+1/2, z+1/2; #7: x-1, -y+1/2, z-1/2; #8: -x+1, y+1/2, -z+1/2; #9: x, -y+1/2, z-1/2.

S6. The bond valence sum calculations of Fe for LCU-101 and LCU-102.

Table S4 The bond valence sum calculations of Fe for **LCU-101.**

Fe(1)-O(2)	2.014	0.469186
Fe(1)-O(7)	2.36	0.184171
Fe(1)-O(8)	2.124	0.348522
Fe(1)-O(10)	1.998	0.48992
Fe(1)-O(15)	2.156	0.319646
Fe(1)-O(16)	2.2	0.283807
$V_{\mathbf{Fe(1)}}$ = 2.10		
Fe(2)-O(4)	2.017	0.465397
Fe(2)-O(5)	2.102	0.369873
Fe(2)-O(6)	2.259	0.241975
Fe(2)-O(11)	2.075	0.397873
Fe(2)-O(13)	2.102	0.369873
Fe(2)-O(14)	2.326	0.201897
$V_{\mathbf{Fe(2)}}$ = 2.05		
Fe(3)-O(1)	2.082	0.390417
Fe(3)-O(8)	2.184	0.296349
Fe(3)-O(9)	2.113	0.359039
Fe(3)-O(17)	2.059	0.415456
Fe(3)-O(18)	2.204	0.280756
Fe(3)-O(22)	2.169	0.30861
$V_{\mathbf{Fe(3)}}$ = 1.74		
Fe(4)-O(3)	2.107	0.364909
Fe(4)-O(12)	2.096	0.37592
Fe(4)-O(13)	2.187	0.293956
Fe(4)-O(20)	2.179	0.300381
Fe(4)-O(21)	2.093	0.378981
Fe(4)-O(26)	2.139	0.334675
$V_{\mathbf{Fe(4)}}$ = 1.71		

$$V_M = \sum_j S_{M-O_j} = \sum_j \exp\left(\frac{r_0 - r_{M-O_j}}{0.37}\right) ; \; r_{\mathrm{Fe}^{\mathrm{II}}-\mathrm{O}} = 1.734\ \text{Å}.$$

Table S5 The bond valence sum calculations of Fe for **LCU-102.**

Fe(1)-O(1)	2.196	0.286892
Fe(1)-O(2)	2.15	0.324872
Fe(1)-O(7)	2.006	0.479441
Fe(1)-O(10)	1.98	0.514343
Fe(1)-O(13)	2.186	0.294752
Fe(1)-O(14)	2.144	0.330183
$\boldsymbol{V}_{\mathbf{Fe(1)}} = 2.23$		
Fe(2)-O(3)	1.949	0.559293
Fe(2)-O(5)	2.165	0.311965
Fe(2)-O(6)	2.17	0.307777
Fe(2)-O(11)	2.119	0.353264
Fe(2)-O(12)	2.228	0.263123
Fe(2)-O(15)	1.975	0.521341
$\boldsymbol{V}_{\mathbf{Fe(2)}} = 2.32$		

$$V_M = \sum_j S_{M-O_j} = \sum_j \exp(\frac{r_0 - r_{M-O_j}}{0.37})\text{ ; } r_{\mathrm{Fe}^{\mathrm{II}}\text{–O}} = 1.734\ \text{Å}.$$